Transformation of Neutral Rhenium Compounds During Electrospray Ionization Mass Spectrometry

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Four neutral rhenium compounds were examined by electrospray ionization mass spectrometry. Acetonitrile solutions of (Ind)Re(CO)$_3$ (Ind = indenyl) and (Cp)Re(CO)$_3$ (Cp = cyclopentadienyl) gave rise to $[Re(CO)_3(CH_3CN)_3]^+$ ions. This is indicative of a reaction with the solvent, although these compounds do not react with acetonitrile under regular laboratory conditions. In contrast, (Ind)Re(CO)$_2$(butyne) and (Cp)Re(CO)$_2$(butyne) did not lose their aromatic hydrocarbon ligand upon ionization; the predominant product ions generated upon electrospray ionization were $[(Ind)Re(CO)(CH_3CN)(butyne)]^+$ and $[(Cp)Re(CO)(CH_3CN)(butyne)]^+$, respectively. © *1997 American Society for Mass Spectrometry (J Am Soc Mass Spectrom 1997, 8, 191–194)*

Introduction

During the last 10 years it has been shown that electrospray ionization mass spectrometry (ESI-MS) is an extremely valuable technique for analysis of high molecular weight biomolecules as well as low molecular weight organic compounds [1]. In general, electrospray ionization (ESI) mass spectra provide the molecular weight of the compounds and tanden mass spectrometry (MS/MS) experiments yield structural information. In contrast, less attention has been paid to the use of ESI-MS in the area of organometallic chemistry [2]. The field of organometallic chemistry has been one of the most active areas of chemical research in recent years, being fueled by its importance for many industrial processes, for example, catalysis. Obviously, mass spectrometry is an important tool for characterization of organometallic compounds. Frequently, electron impact (EI) is the ionization method of choice because of its sensitivity and simplicity. However, ESI should be explored as well because it has the advantage that it can handle (dilute) solutions. Analysis of salts of organometallic compounds is relatively straightforward [2] and it has been shown that intense $[M + H]^+$ ions are generated for a number of organometallic compounds having protonatable sites on one of the ligands [3]. In general, analysis of neutral organometallic compounds of low basisity has been more problematic with ESI. Neutral metallocenes are oxidized, generating M^+ ions [4], because the ESI source is an electrochemical cell [5]. Alternatively, neutral compounds, such as metal carbonyls, can be ionized by adding Ag^+ or H_3CO^- ions to the solution [6]. In contrast to these examples, data will be presented here for four neutral rhenium compounds (**1**–**4**) that are structurally transformed during the ESI process. Although ionization of biopolymers by ESI seems to be an inert process, the electrochemical nature of the ESI source combined with the susceptibility of organometallic compounds to redox reactions forces chemists to be cautious while interpreting ESI data for these compounds. In this study four neutral rhenium compounds (**1**–**4**) will be examined. These four rhenium compounds were synthesized to investigate substitution reactions of cyclopentadienyl (Cp) or indenyl (Ind) rhenium carbonyl compounds. The mechanism of these reactions involves ring slippage of the Cp or Ind ligand from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1/\eta^5$ to promote an associative mechanism [7].

Experimental

Mass Spectrometry

A VG AutoSpec triple sector (EBE) mass spectrometer (Micromass Ltd., Manchester, UK), equipped with a Mark II electrospray source [8], was used to obtain all regular ESI mass spectra. The needle was made of steel and carried a potential of 4 kV relative to the accelerat-

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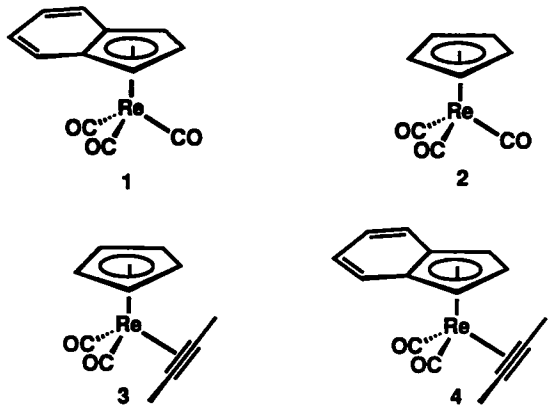

ing voltage (4 kV). The experiments were performed in the positive ion mode and with a resolution of 1500 (10% valley definition). The sampling cone voltage was varied to study its influence on the mass spectra. The samples were dissolved in CH_3CN (about 200 ng μL^{-1}) and introduced into the mass spectrometer by continuous infusion (15 μL min^{-1}). N_2 was used as both the nebulizer and the bath gas. A Sciex (Concord, Ontario) API III Plus triple quadrupole mass spectrometer was used to obtain the tandem and triple mass spectra. The samples were dissolved in CH_3CN and the flow rate was 2 μL min^{-1}. N_2 was used as the nebulizer gas and the curtain gas; Ar was the collision gas. (For more details, see [9].)

Materials

Detailed information about the synthesis of **1**, **2**, **3**, and **4** is available from refs 10, 11, 12, and 7c. The identity of these compounds was confirmed by NMR spectroscopy and EI mass spectrometry. No impurities were detected. Anhydrous acetonitrile in a Sure/Seal™ bottle was purchased from Aldrich Chemical Co. (Milwaukee, WI).

Results and Discussion

The ESI mass spectrum of **1** in CH_3CN is shown in Figure 1 and the spectrum is dominated by ions at m/z 394. (For brevity, all the ions identified are the more abundant ^{187}Re-containing species.) If **1** was ionized intact, ions at m/z 386 (1^+) should have been present. These types of rhenium compounds are known to be stable in acetonitrile, as well as most other organic solvents, for days. Therefore, a reaction must have occurred during the ESI process. The isotope pattern reveals that the ions at m/z 394 contain one rhenium atom. Because only CH_3CN, N_2 and **1** are

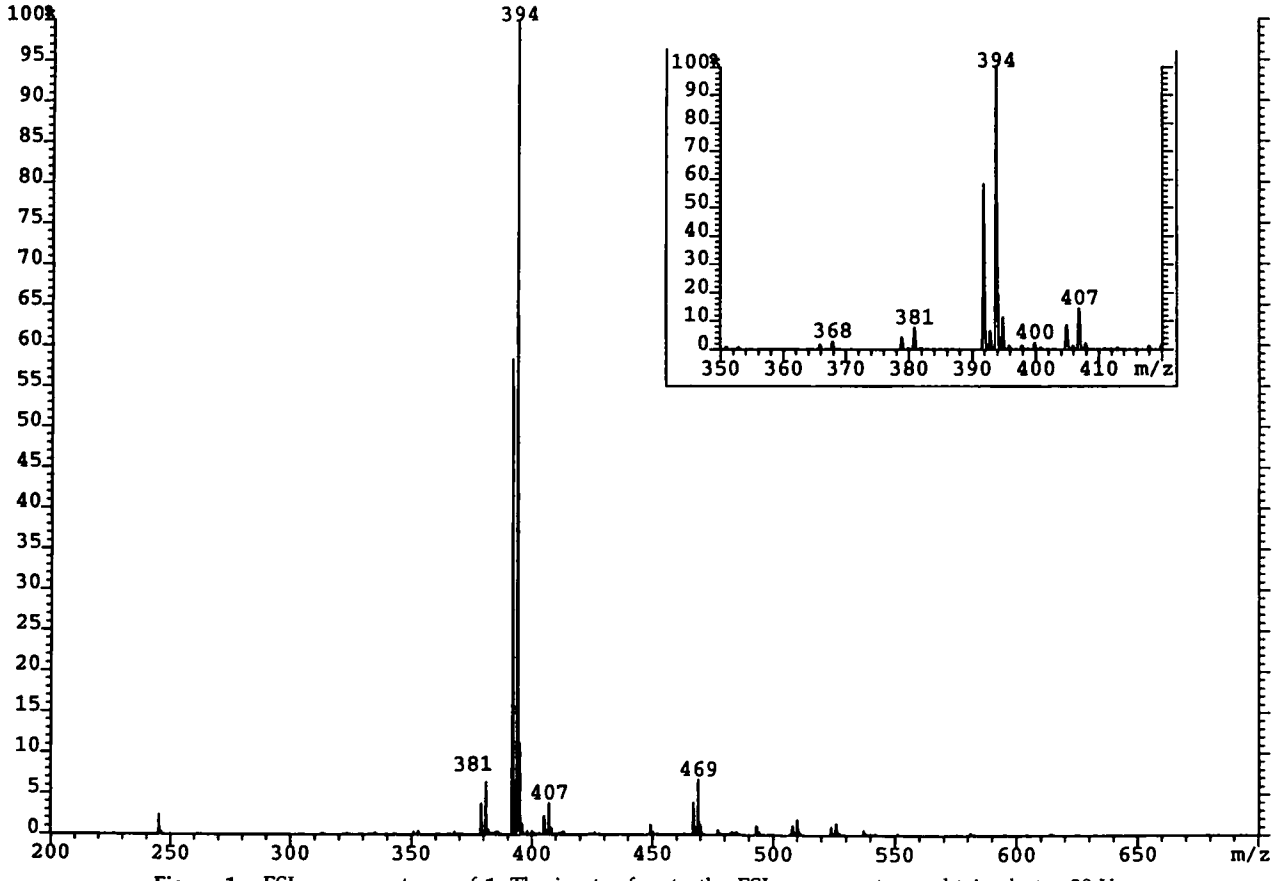

Figure 1. ESI mass spectrum of **1**. The inset refers to the ESI mass spectrum obtained at a 20-V higher sampling cone voltage. See Experimental section for details.

Table 1. Tandem mass spectrum of the m/z 394 ions generated by **1** upon ESI

m/z	Intensity	Assignment
312	43	$-2\ CH_3CN$
284	75	$-2\ CH_3CN,\ -CO$
271	100	$-3\ CH_3CN$
256	80	$-2\ CH_3CN,\ -2\ CO$
243	13	$-3\ CH_3CN,\ -CO$

present during ESI, it seems reasonable to assign the ions at m/z 394 to $[Re(CO)_3(CH_3CN)_3]^+$. This assignment is confirmed by the tandem mass spectrum of m/z 394 obtained with a triple quadrupole mass spectrometer (see Table 1) [9]. All the ions observed in the tandem mass spectrum can be assigned to multiple losses of 28 (CO), 41 (CH_3CN), or a combination of them. A metastable ion kinetic energy (MIKE) spectroscopy experiment was also performed with the VG AutoSpec (EBE). In this experiments the m/z 394 ions were mass-selected (EB) and guided through a collision cell filled with helium followed by analysis of the fragment ions (E). The most abundant ion in the MIKE spectrum is m/z 353 ($[M - CH_3CN]^+$), followed by m/z 312 ($[M - 2\ CH_3CN]^+$) and m/z 325 ($[M - CH_3CN - CO]^+$). The differences between the tandem mass spectrum obtained by using MIKE spectroscopy with the AutoSpec and that obtained with the triple quadrupole mass spectrometer are presumably a function of the number of collisions and/or the collision energy. An MS/MS/MS experiment was performed with the triple quadrupole mass spectrometer by generating m/z 284 ions from the parent ions (m/z 394) in the ion source (increased orifice potential) and mass selecting the m/z 284 ions (Q1) for subsequent collision-induced dissociation (Q2) and mass analysis of the fragments (Q3). This spectrum contains ions at m/z 256 ($[M - CO]^+$), 228 ($[M - 2\ CO]^+$), 215 ($[M - CO - CH_3CN]^+$), and 187 ($[M - 2\ CO - CH_3CN]^+$, Re^+). Thus, during ESI of compound **1** the indenyl ligand is replaced with three acetonitrile molecules, which are known to be good ligands for transition metals. Note that $[Re(CO)_3(CH_3CN)_3]^+$ is a stable 18 electron system, whereas $\mathbf{1}^+$ is a labile 17 electron system. Thus, we suggest that, after generation of labile $\mathbf{1}^+$ ions by oxidation of **1**, the rhenium atom is attacked by one acetonitrile molecule, which induces ring slippage of the indenyl ligand ($\eta^5 \rightarrow \eta^3$). This is followed by loss of the indenyl ligand and incorporation of two additional acetonitrile molecules, generating $[Re(CO)_3(CH_3CN)_3]^+$ ions. The tandem mass spectrum indicates that CO is more strongly bound than CH_3CN.

At a 20-V higher sampling cone voltage (more intense) ions at m/z 368, 381, and 407 appeared in the ESI mass spectrum of **1** in CH_3CN (see inset in Figure 1). These ions can be assigned to $[Re(CO)_5(CH_3CN)]^+$, $[Re(CO)_4(CH_3CN)_2]^+$, and $[Re(CO)_2(CH_3CN)_4]^+$, respectively. The tandem mass spectrum of the m/z 381 ions is presented in Table 2 and it confirms the structural assignment. These data indicate that the CO and CH_3CN ligands can be interchanged relatively easily during electrospray with the energy transferred during the collisions acting as the driving force.

The ESI mass spectrum of **2** (not shown) is similar to that of **1**; both spectra are dominated by m/z 394, and MS/MS and MIKE spectroscopy experiments indicate that these ions have the $[Re(CO)_3(CH_3CN)_3]^+$ structure.

The ESI mass spectrum of **3** is dominated by m/z 375. Generation of intact $\mathbf{3}^+$ ions should have produced m/z 362 ions. Although a small signal at m/z 362 is visible, it is only 8% of that at m/z 375. There are also relatively weak signals at m/z 347, 425, and 445, but their origin is unknown. Tentatively, the ions at m/z 375 correspond to $[(Cp)Re(CO)(CH_3CN)(C_4H_6)]^+$ or $[(Cp)Re(CH_3CN)_3]^+$, both 17 electron species. The MIKE spectrum of m/z 375 provides the information to distinguish between these two structures. The latter spectrum contains structure characteristic signals at m/z 321, 306, and 280, which correspond to loss of C_4H_6, $CH_3CN + CO$, and $CH_3CN + C_4H_6$, respectively. In addition, there is no signal at m/z 293 (loss of two CH_3CN) although m/z 334 is the base peak in the spectrum (loss of CH_3CN). Thus, the m/z 375 ions most likely have the $[(Cp)Re(CO)(CH_3CN)(C_4H_6)]^+$ structure, which indicates that one of the carbon monoxide ligands in **3** was replaced by an acetonitrile molecule during ESI.

The chemistry of **3** differs from that of **1** and **2** in the sense that the aromatic hydrocarbon ligand remains attached to the rhenium atom. Because butyne can act as a four electron as well as a two electron donor [13], $\mathbf{3}^+$ is probably less vulnerable to attack by acetonitrile molecules. The same applies to **4**, although the only difference with **1** is a C_4H_6 ligand instead of a third CO ligand. The base peak in the ESI mass spectrum of **4** is m/z 425 and this signal can be ascribed to $[(Ind)Re(CO)(CH_3CN)(C_4H_6)]^+$ or $[(Ind)Re(CH_3CN)_3]^+$. MIKE spectroscopy data suggest that the former structure is more likely. Another prominent signal appears at m/z 385, which could possibly correspond to $[(Ind)Re(CH_3CN)_2H]^+$.

Thus, a few examples have been presented of rhenium compounds that are transformed during the electrospray process. The exact nature of the processes is under investigation. More rhenium compounds will be examined to rationalize the data in greater detail and

Table 2. Tandem mass spectrum of the m/z 381 ions generated by **1** upon ESI

m/z	Intensity	Assignment
312	23	$-CH_3CN,\ -CO$
284	71	$-CH_3CN,\ -2\ CO$
271	100	$-2\ CH_3CN,\ -CO$
256	62	$-CH_3CN,\ -3\ CO$
243	8	$-2\ CH_3CN,\ -2\ CO$

to observe trends, but it is already clear that the nature of the ligands determines the reactivity. The acetonitrile solvent molecules are probably the driving force after generation of intact molecular ions for the rhenium compounds. We plan to exploit the observed reactions to generate novel organometallic complexes and study their behavior in the gas phase.

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